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Effect of Annealing Treatment on the Microstructure and Properties of Cold-Sprayed Cu Coating

Wen-Ya Li, Chang-Jiu Li, and Hanlin Liao

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Copper (Cu) coating was deposited by cold spraying, and the electrical resistivity of the coating in both directions parallel and perpendicular to the coating surface was measured to investigate the anisotropy of the coating. Annealing treatment was applied to the coating to examine its effect on the microstructure and properties of the cold-sprayed Cu coating. The examination of coating microstructure evidently revealed that the coating was constituted by the flattened particles, and the interfaces were clearly observed between the deposited particles. The anisotropy in microstructure and electrical resistivity was present in cold-sprayed Cu coating. The electrical resistivity of the as-sprayed coating was higher than that of Cu bulk. Moreover, the electrical resistivity along the direction parallel to the coating surface was lower than that along the perpendicular direction. It was found that annealing treatment led to the enhancement of particle interface bonding and evident recrystallization of the elongated grains and remarkable grain growth as well. The annealed coating presented equiaxed grain structures similar to the annealed Cu bulk with particle interfaces almost disappearing under certain annealing conditions The coalescence of voids or pores in the coating was clearly observed at high annealing temperatures. Moreover, the annealed coating yielded an electrical resistivity and microhardness comparable to Cu bulk.

Keywords annealing treatment, cold spraying, copper (Cu) coating, electrical resistivity, microhardness, microstructure

1. Introduction

In the cold-spraying process, spray particles are injected into a supersonic jet in a de Laval type nozzle and accelerated to a high velocity (300–1200 m/s). The deposition of particles takes place through the intensive plastic deformation upon impact in a solid state at a temperature well below the melting point of spray material. Consequently, the deleterious effects of oxidation, phase transformation, decomposition, grain growth, and other problems inherent in the conventional thermal spraying can be minimized or eliminated (Ref 1). However, a cold-spray coating consists of particles deformed to a lens-like shape. The orientation of deformation of the particles and the incompleteness of interface bonding between the deposited particles may result in an anisotropy of coating microstructure and lower mechanical strength and both electrical and thermal conductivities.

For thermally sprayed coatings, heat treatment can be applied to release the residual stress, decrease porosity, or to improve the properties of coatings (Ref 2). Recent examination of the microstructure of cold-sprayed coating revealed that a metastable structure was evolved at the interface area between the deposited particles, which resulted from the intensive deformation of particles upon impact (Ref 3-5). Due to the lower thermal stability of metastable phases evolved at the interfaces in cold-sprayed coating, the postannealing treatment may provide an approach to modify the microstructure and properties of cold-spray coating. Several reports have demonstrated the effect of annealing on the properties of cold sprayed coatings (Ref 6-8). Moreover, it is of interest that the internal fatigue microcracks of engineering materials could be “healed” through annealing treatment (Ref 9). Therefore, it may be expected to heal the incompleteness of interface bonding in a cold-sprayed coating. Consequently, the properties of the coating could be modified.

Cold-sprayed copper (Cu) coating has been used in industrial applications due to its excellent electrical (Ref 10) and thermal conductivity (Ref 11). Therefore, it is expected to modify the coating properties through development of the microstructure of Cu coating. In the present paper, Cu coating was deposited by cold spraying. The effects of annealing conditions on the microstructural evolution, electrical resistivity, and microhardness of the coating were examined.

2. Materials and Experimental Procedures

Commercially available Cu powder (−48 μm) was used as feedstock; it has a spherical morphology (Fig. 1a). The measurement yielded a particle size distribution of $d(0.1)$ = 11.2 μm,

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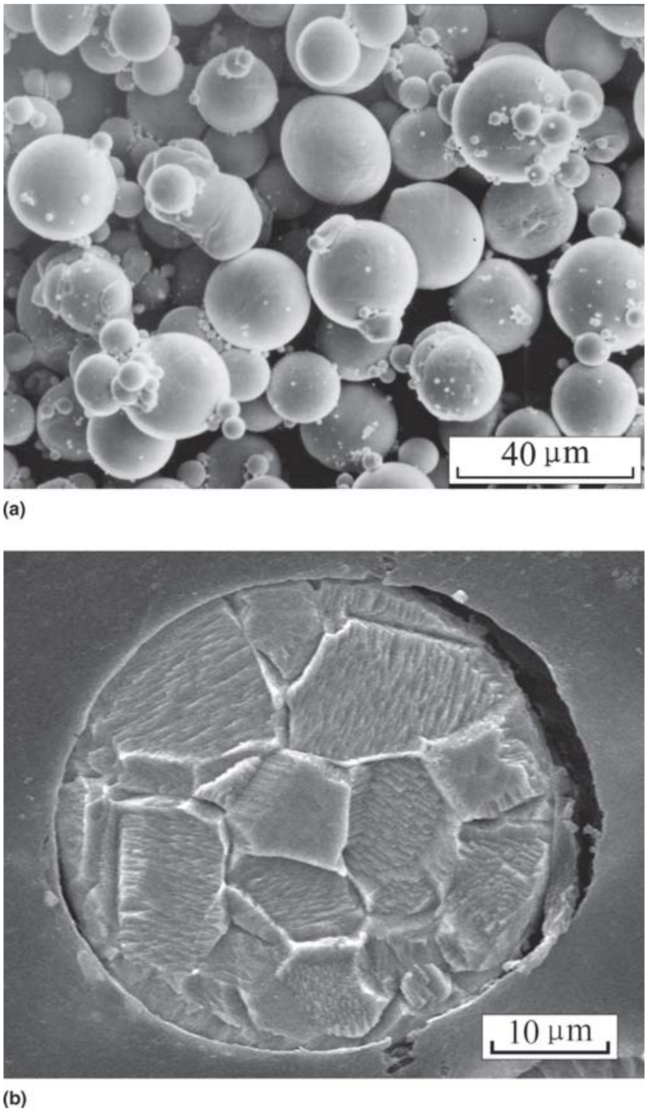

Fig. 1 SEM morphology of (a) Cu powder and (b) the etched cross section of a particle

$d(0.5) = 23.3$ μm, and $d(0.9) = 41.6$ μm. The size of grain in powder particle was around 10 μm, observed from the cross-sectional microstructure of powder after etching (Fig. 1b). The etching aqueous solution used in the current study was composed of 5 g $FeCl_3$ + 10 mL HCl + 100 mL H_2O. The test using an oxygen determinator (RO-316, LECO, MI) yielded an oxygen content of about 0.04 wt.% for Cu powder. Cold-rolled Cu plate was used as a substrate. Prior to spraying, the substrate surface was sandblasted using 24 mesh alumina grits.

A home-installed cold-spraying system developed in Xi'an Jiaotong University was used to produce Cu coating. A converging/diverging de Laval nozzle of a conical shape was adopted. The expansion ratio of the nozzle was 9 and the downstream length from the throat to the exit was 100 mm. The detail of the system construction has been described elsewhere (Ref 12). N_2 was used as the driving gas operating at a pressure of 2 MPa and a temperature of about 150 °C in the prechamber. N_2 was also used as powder carrier gas. The standoff distance from the nozzle exit to the substrate surface was 15 mm. During deposition, the spray gun was manipulated by a robot and traversed at a speed of 80 mm/s.

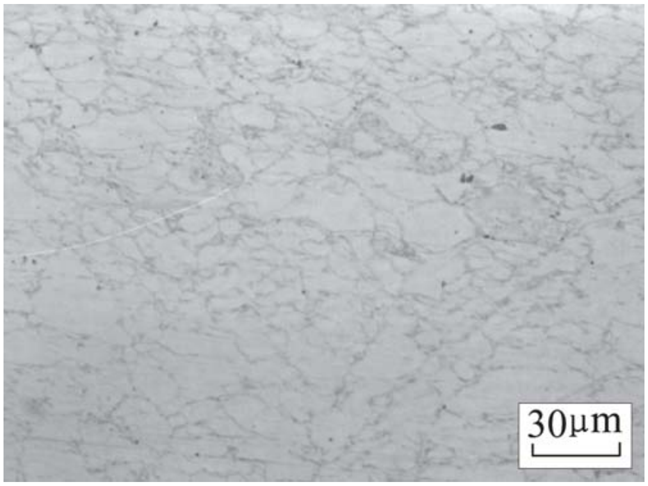

Fig. 2 Typical microstructure of the as-sprayed Cu coating

According to the experimental data in the literature (Ref 13), the strength and hardness of Cu bulk change significantly at the annealing temperatures between 200 and 400 °C and change little at the annealing temperatures between 550 and 800 °C. Therefore, in this study, the annealing treatment was conducted in an electrical furnace at two temperatures of 350 and 650 °C for different times under N_2 atmosphere.

The microstructure of cold-sprayed Cu coating before and after annealing was characterized using optical microscopy (OM; MeF3A, Reichert-Jung, Wetzlar, Germany), scanning electron microscopy (SEM; S-2700, Hitachi, Tokyo, Japan). Because of the dense microstructure of cold-sprayed Cu coating, the individual deformed Cu particles cannot be clearly observed in a polished state. Therefore, the as-polished cross section of Cu coating was etched using the same etching solution as that used for powder for microstructure examination.

Microhardness of the coating was tested by a Vickers hardness tester under a load of 200 g and a loading time of 15 s. More than 10 tests were made on a polished cross section of specimen, and the average value was used as an indicator of coating microhardness.

The electrical resistivity of the coating in both directions parallel and perpendicular to coating surface was tested using Kelvin double bridge circuit. The coating was deposited to a thickness of about 7 mm for the test of electrical resistivity in the perpendicular direction. After deposition, the coating was machined to the samples of square cross section of 1 × 1 mm by electrical discharge machining.

3. Results and Discussion

3.1 Anisotropy of Microstructure and Electrical Resistivity

Figure 2 shows a typical microstructure of the as-sprayed Cu coating. It is clear that a dense Cu coating was formed by cold

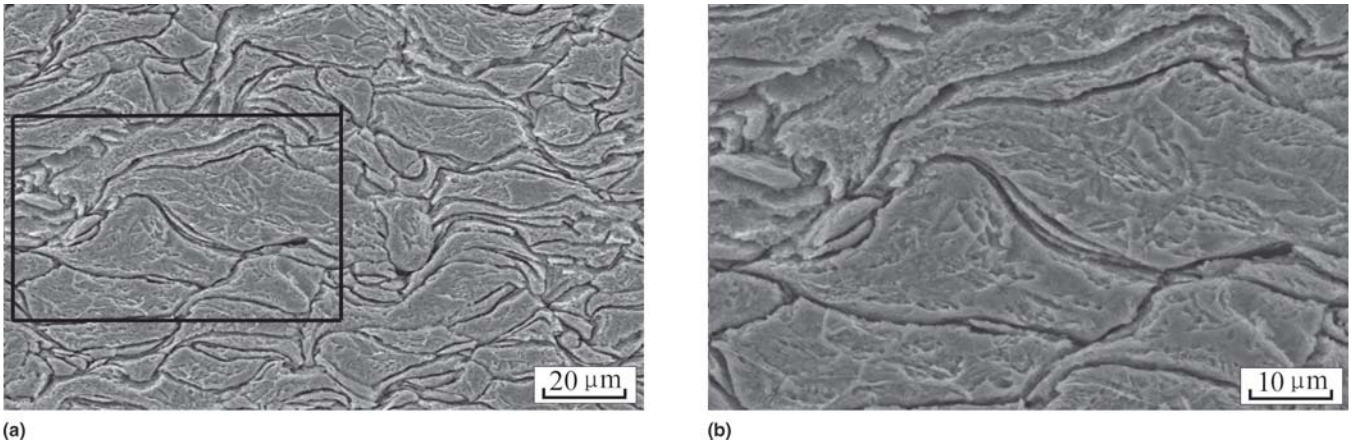

Fig. 3 Typical microstructure of the as-sprayed Cu coating (a) low magnification; (b) high magnification

spraying. The interface boundaries between deposited particles were vaguely observed. The measurement yielded the oxygen content in the coating comparable to that in the feedstock. This means that the oxidation during spraying was negligible. This result is consistent with that reported in Ref 5 and 8. Figure 3 shows a typical microstructure of the etched cross section of the as-sprayed Cu coating observed by SEM. It is clear that the deposited particles have experienced intensive deformation and deformed to an elongated shape. At a high magnification, it was observed (Fig. 3b) that the deformation of particle was more concentrated on the interparticle boundaries. After etching, all particle boundaries were more clearly revealed. This means that particle boundary is more easily etched than bulk inside of particle. This implies the deposited particles may be only weakly bonded together.

Moreover, it was clear from the morphology of deposited particles that anisotropy was present in microstructure, especially in the directions parallel and perpendicular to the deformation flow direction. Consequently, the properties of cold-sprayed Cu coating may be influenced by this anisotropy microstructure feature.

The measurement of electrical resistivity of the as-sprayed Cu coating yielded mean values of 2.15 and 3.8 μΩ cm along the directions parallel and perpendicular to the coating surface, respectively. The electrical resistivity at the direction parallel to coating surface was comparable to those reported by Borchers et al. (Ref 6) and by McCune et al. (Ref 8). The electrical resistivity at the direction perpendicular to coating surface was 1.8 times higher than along coating surface direction. It is evident that this anisotropy of electrical conductivity resulted from coating microstructure features.

3.2 Evolution of Coating Microstructure during Annealing Treatment

Generally, as cold-worked metallic materials are annealed, the recovery, recrystallization, and grain growth occur in different time stages at a given temperature (Ref 14). Figure 4 shows the microstructures of the Cu coating annealed at 350 °C for 4 and 36 h. After 4 h annealing, it was found that the obvious recrystallization has occurred in the coating, especially the elongated grains at the interfaces. The grain size was comparable to that in feedstock. Decker et al. (Ref 7) and McCune et al. (Ref 8) also reported this phenomenon. The close examination of coating microstructure (Fig. 4b) indicates that the healing up of weakly bonded interfaces occurred through interface diffusion during annealing to form a metallurgical bonding as marked by arrows. It is similar to that occurring in solid state diffusion bonding process (Ref 15, 16).

As the coating was annealed for 36 h at 350 °C, more evident strong bonding can be clearly observed (Fig. 4d). According to the principle of solid-state diffusion bonding (Ref 15, 16) and the results on healing of the internal fatigue microcracks of engineering metallic materials through annealing treatment reported by Zhang et al. (Ref 9), it can be considered that the fraction of metallurgical bonding area at interfaces increases with increasing annealing time.

Therefore, to speed up the healing process of the interface boundary, the annealing treatment was performed at a higher temperature of 650 °C. Figure 5(a) shows the microstructure of the coating annealed at 650 °C for 1 h. Although the healing was not complete and some interface areas delineated by etching were still clearly observed, the lamellar feature observed on a cross section of the as-sprayed coating became not clear. On the other hand, sphericization of interface voids or pores and formation of the twin grains were clearly observed. This means that the diffusion across particle interface and recrystallization within deposited particles took place significantly. As annealing progresses, the atomic diffusion between the well-bonded particles gradually heals the weakly bonded interfaces. Although the formation of twin grains was clearly observed, the grain size in this annealed Cu coating was comparable to that in the original Cu powder.

Figure 5(b) shows the microstructure of the coating annealed at 650 °C for 12 h. It presented a completely different microstructure from the as-sprayed coating. The equiaxed grains were evolved in the coating instead of elongated grains in the as-sprayed coating. The grain size in the coating annealed at 650 °C for 12 h (Fig. 5b) was much larger than that in feedstock (Fig. 1b). Many twins were also present in the annealed coating. Moreover, particle boundaries were no longer observed from the cross section and the grain boundaries were observed.

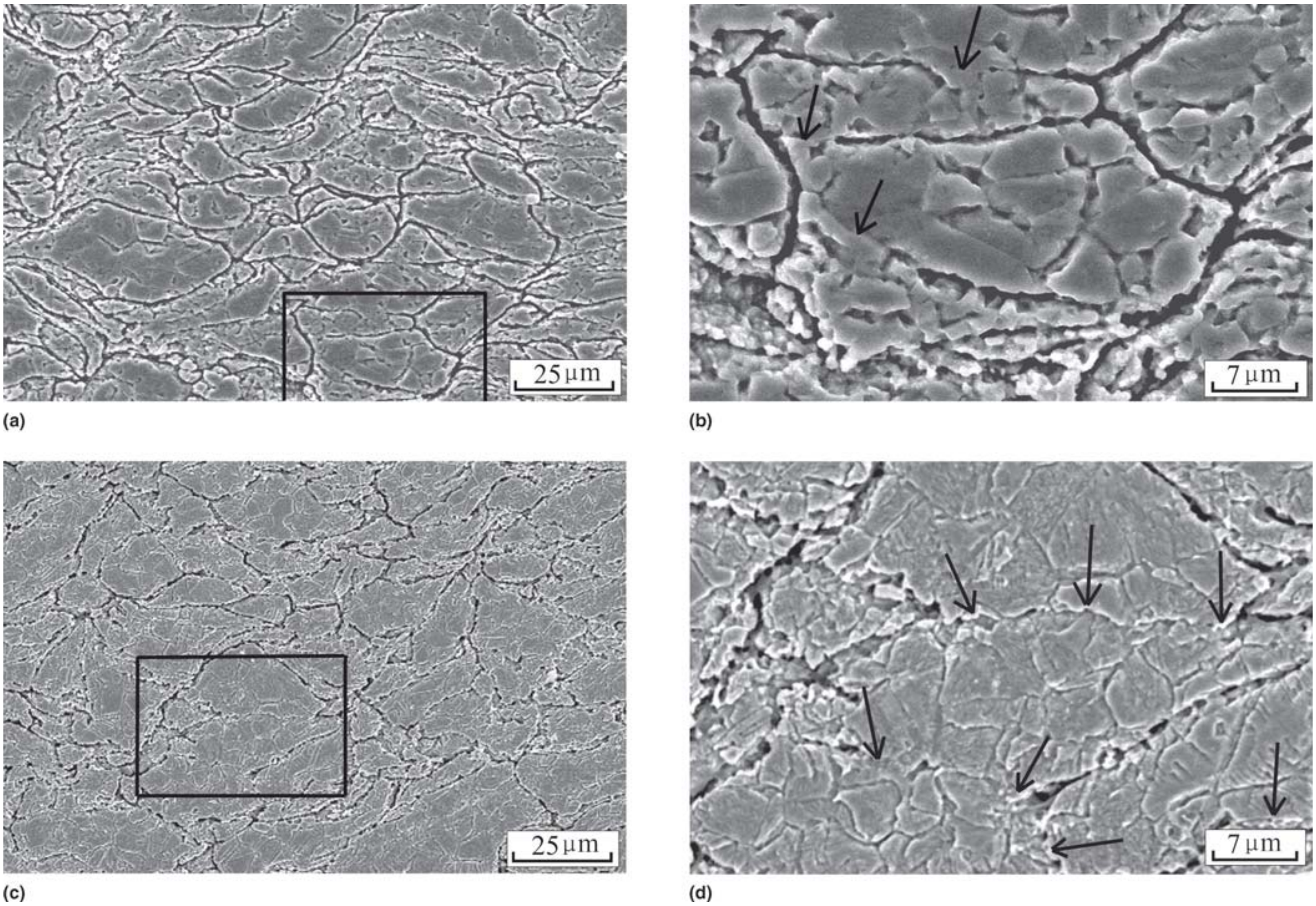

Fig. 4 Typical microstructures of Cu coating annealed at 350 °C for (a) and (b) 4 h and (c) and (d) 36 h

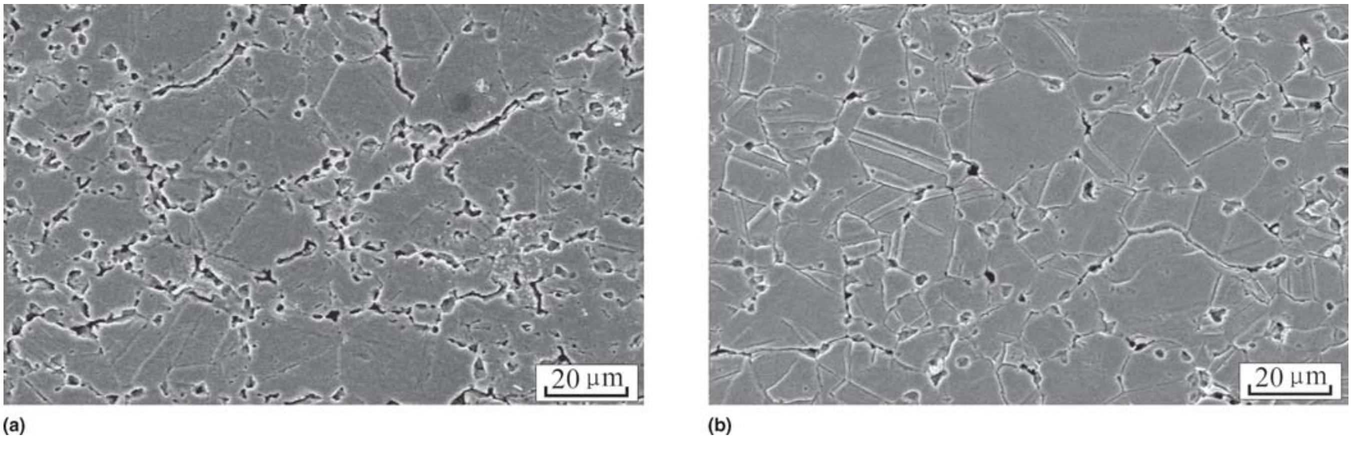

Fig. 5 Typical microstructures of Cu coating annealed at 650 °C for (a) 1 h and (b) 12 h

According to the results reported by Zhang et al. (Ref 9), the interface voids appearing as unbonded interfaces in this study will tend to be sphericized. It was reported that under solid-state diffusion bonding, the oxide films between particles will also be coalesced and sphericized as the grain grows during annealing (Ref 15). As shown in Fig. 5(b), the coalescence of voids or pores between nonbonded interfaces can clearly be seen accompanying the apparent grain growth at an elevated annealing temperature. Moreover, it is of interest that McCune et al. (Ref 8) observed the sphericization of oxide film in cold-sprayed Cu coating after annealing under vacuum condition. The volume fraction of these etched craters in Fig. 5(b) was estimated to be

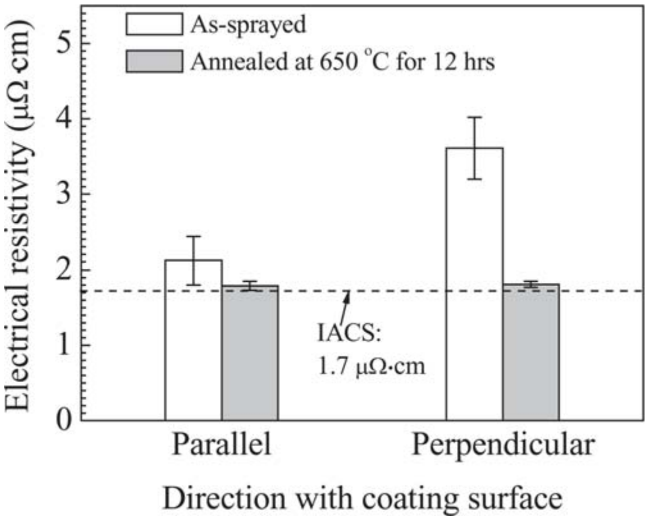

Fig. 6 Effect of annealing on the electrical resistivity of cold-sprayed Cu coating in the parallel and perpendicular directions

about 2%. Those results reveal that the unbonded interfaces between the deposited particles could be taken as the microcracks in the coating, which can be healed through the postspraying annealing. Therefore, the anisotropy microstructure of cold-sprayed coating could be eliminated through annealing treatment.

3.3 Effect of Annealing on Electrical Resistivity of the Coating

The electrical resistivity of the cold-sprayed Cu coating in the direction parallel to coating surface (referred as parallel direction) has been reported to be 1.7 ± 0.3 μΩ cm and 2.8 μΩ cm by Borchers et al. (Ref 5, 6) and 2.4 μΩ cm by McCune et al. (Ref 8), although it is obvious that Borchers et al. (Ref 6) made a mistake in their later report by one order of magnitude. Those data are comparable with the results obtained in this study. However, there were no data for the electrical resistivity of the coating in the direction perpendicular to coating surface (referred to as perpendicular direction). Figure 6 shows the electrical resistivity of the cold-sprayed Cu coating after annealing treatment compared with the as-sprayed one in both parallel and perpendicular directions obtained in this study. Compared with the electrical resistivity of annealed Cu bulk [International Annealed Copper Standard (IACS), 1.7 μΩ cm at 20 °C], it is clear that the electrical resistivity of the cold-sprayed Cu coating was a little higher. The mean electrical resistivity of the as-sprayed Cu coating was about 26.5% higher in the parallel direction and about 124% higher in the perpendicular direction than that of IACS bulk copper.

For the Cu coating annealed at 650 °C for 12 h, the mean electrical resistivity was only about 5.3% and 6.5% higher in the parallel and perpendicular directions, respectively, than that of the IACS bulk copper. This clearly indicates that the electrical resistivity of cold-sprayed Cu coating can be significantly reduced through annealing treatment. This result is consistent with the result reported by Borchers et al. (Ref 6). Moreover, the present results revealed that the anisotropy in electrical resistivity almost disappears with the elimination of anisotropy in microstructure. Therefore, the annealing treatment can significantly improve the properties of cold-sprayed Cu coating accompanying the homogenized microstructure.

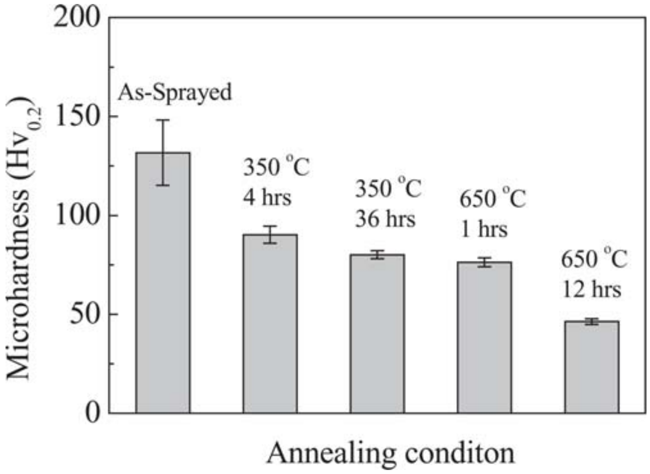

Fig. 7 Effect of annealing condition on the microhardness of cold-sprayed Cu coating

3.4 Effect of Annealing Conditions on Microhardness of Cu Coating

The microhardness of the as-sprayed and annealed Cu coating is shown in Fig. 7. The microhardness of the as-sprayed Cu coating was about 132 $\mathrm{Hv}_{0.2}$, which was consistent with those reported by Borchers et al. (Ref 5, 6) and McCune et al. (Ref 8). This value was much higher than that of the annealed Cu bulk due to the strain-hardening effect during deposition. After annealing, the microhardness of the cold-sprayed Cu coating decreased significantly with increasing annealing temperature. This fact agrees with the results reported recently by Borchers et al. (Ref 6). However, the microhardness of coating was not reduced significantly with increasing holding time as annealed at 350 °C. This is because the grain growth rate was low at a relatively low temperature, although the recrystallization has completely taken place. After annealing at 650 °C, the microhardness of the coating clearly decreased with increasing holding time. At 1 h annealing, the coating yielded a microhardness of 76.3 $\mathrm{Hv}_{0.2}$, which was comparable to that reported by Borchers et al. (Ref 6) for the Cu coating annealed at 600 °C for 1 h. However, the microhardness of the coating became about 46 $\mathrm{Hv}_{0.2}$ after annealing at 650 °C for 12 h. This result is comparable to that of annealed bulk copper. Borchers et al. argued that the maintain of the higher hardness of Cu coating annealed at 600 °C for 1 h than annealed bulk copper is due to the persistence of the generated dislocation loops during coating deposition (Ref 6). This possibly resulted from a short annealing time because the present results clearly revealed that after annealing at 650 °C for 12 h, the microhardness of the coating reduced to a value comparable to annealed bulk copper. Therefore, it can be considered that the persistent dislocation loops in the cold-sprayed Cu coating can be removed through annealing for a slightly longer time. The present results suggest that the removal of dislocation loops may also contribute to an increase of Cu coating electrical conductivity. This is because the electrical resistivity of the annealed cold-sprayed Cu coating at 600 °C for 1 h reported by Borchers et al. (Ref 6) was about 1.9 μΩ cm, which is 12% higher than the IACS bulk copper and also about 5% higher than that of the annealed Cu coating at 650 °C for 12 h in this work.

These results clearly show that the microstructure and properties of cold-sprayed coating can be influenced significantly by the annealing conditions. Therefore, the annealing treatment provides an approach to control the coating microstructure and properties. Moreover, as the microhardness of the cold-sprayed coating can be modified through annealing treatment, it is expected that the adhesion and cohesion of cold-sprayed coating could be improved through the healing of nonbonded interfaces. A study focusing on this aspect is in progress.

4. Conclusions

A dense Cu coating was produced by cold spraying with a high microhardness caused by the strain-hardening effect during deposition. The as-sprayed coating was made up of the flattened particles. The anisotropy in microstructure and electrical resistivity was present in the as-sprayed Cu coating. The electrical resistivity of the as-sprayed Cu coating was higher than that of Cu bulk. Moreover, the electrical resistivity along the direction parallel to the coating surface was lower than that along the perpendicular direction. On the other hand, it was found that the annealing improves the interface bonding between the deposited particles. The annealing led to the evident recrystallization of the deformed grains and remarkable grain growth as well at elevated temperature. The annealed coating presented an equiaxed grain structure similar to the annealed Cu bulk with particle interfaces almost disappearing under certain annealing conditions. The coalescence of voids or pores in the coating was clearly observed at a relatively high annealing temperature and long holding time. Furthermore, the annealed coating yielded the electrical resistivity and microhardness comparable to Cu bulk. Therefore, it is clear that the microstructure and properties of the cold-sprayed coating can be significantly modified through postspraying annealing treatment.

Acknowledgments

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